

Temperature mobility of isomeric cluster equilibria: maximizing the effects in the $(\text{CO}_2)_2^-(\text{g})$ isomeric system¹

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Abstract

Theoretical studies indicate that isomerism in molecular clusters is a typical feature of the species, having substantial effects on their thermodynamics and particularly on the heat capacity term. The latter term can be enhanced considerably by isomeric interplay, especially if fast temperature interchange of relative stability of the isomeric structures takes place. Using the example of the $(\text{CO}_2)_2^-(\text{g})$ isomeric cluster system, it is shown how the overall heat capacity enhancement can be maximized with respect to the isomeric energy separation. It is shown that the maximum enhancement amounts to about $136 \text{ J K}^{-1} \text{ mol}^{-1}$ for an energy separation of about 53 kJ mol^{-1} .

INTRODUCTION

Although the possibility of isomerism in molecular complexes formed by weak intermolecular interactions was originally indicated by theoretical means [1,2], there is some experimental evidence, too. The newest observation of such an isomerism is represented by the spectroscopic evidence [3] of two structures in the system $\text{N}_2\text{O}-\text{HF}$. In view of previous experience [4] with thermodynamic consequences of isomerism in other types of systems, it is natural to study the phenomenon with clusters too. Particularly interesting is the case of the heat capacity term, because no a priori upper limit can be imposed upon the effect of isomerism on this term.

PHYSICO-CHEMICAL BACKGROUND

The composition of a two-component ideal gas-phase isomeric system can be described by the mole fractions w_1, w_2 of the two isomers. Here, we shall exclusively deal with equilibrium mixtures. Then, w_i can be expressed

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[4] in terms of partition functions q_i and enthalpy terms at absolute zero temperature $\Delta H_{0,i}^\ominus$, for example

$$w_1 = \frac{q_1}{q_1 + q_2 \exp\left[-(\Delta H_{0,2}^\ominus - \Delta H_{0,1}^\ominus)/RT\right]} \quad (1)$$

Let the index 1 be ascribed to the structure more stable in a low temperature region. Then, in addition to the partial value of a thermodynamic function belonging to the structure itself, the overall term can be considered, corresponding to the equilibrium mixture of both isomers. It is customary [4] to call the difference between the overall and partial terms the isomerism contribution. For example, isomerism contributions to enthalpy and entropy, $\delta H_1^{(\text{iso})}$ and $\delta S_1^{(\text{iso})}$, have been treated quite extensively [4]. The isomerism contribution to enthalpy has the especially simple form

$$\delta H_1^{(\text{iso})} = w_2(\Delta H_2^\ominus - \Delta H_1^\ominus) \quad (2)$$

where ΔH_i^\ominus are the corresponding standard enthalpy terms at a non-zero temperature T .

Essentially, the isomerism contribution to heat capacity related to the structure labelled 1, $\delta C_{p,1}^{(\text{iso})}$, follows from the temperature differentiation of eqn. (2). However, the temperature dependence of not only the ΔH_i^\ominus terms but also of the mole fraction w_2 must be taken into consideration. This is the origin of two components of the $\delta C_{p,1}^{(\text{iso})}$ term

$$\delta C_{p,1}^{(\text{iso})} = w_2(\Delta C_{p,2}^\ominus - \Delta C_{p,1}^\ominus) + w_1 w_2 \frac{(\Delta H_1^\ominus - \Delta H_2^\ominus)^2}{RT^2} \quad (3)$$

where $\Delta C_{p,i}^\ominus$ are standard heat capacity terms at constant pressure corresponding to ΔH_i^\ominus terms.

TEMPERATURE EXTREME OF $\delta C_{p,1}^{(\text{iso})}$

It is evident that the last term in eqn. (3) can reach quite high values, and if we completely disregarded physical bounds, then the term could grow without any limitations. It has been pointed out recently [5] that the temperature dependence of the $\delta C_{p,1}^{(\text{iso})}$ term frequently exhibits a maximum.

Such a feature can be observed with the system [6] of two isomers of $(\text{CO}_2)_2^-(\text{g})$, i.e. the structures of D_{2d} and C_s symmetry point groups. All the parameters necessary for the construction of the partition functions q_i in the rigid-rotor and harmonic-oscillator approximations are available in ref. 6, and the energetics of the system was evaluated [6] using two different approximations, i.e. MP2 and MP3. Table 1 shows that the mole fractions w_i exhibit a quite fast temperature interchange of the relative stability of

TABLE 1

Temperature dependences of the weight factors w_i of the D_{2d} and C_s structures of $(CO_2)_2^-(g)$

T (K)	MP2 ^a		MP3 ^a	
	$w_{D_{2d}}$	w_{C_s}	$w_{D_{2d}}$	w_{C_s}
200	1.0	4×10^{-5}	0.987	0.013
298.15	0.988	0.012	0.622	0.378
400	0.792	0.208	0.173	0.827
500	0.382	0.618	0.057	0.943
600	0.154	0.846	0.026	0.974

^a The approximations are specified in ref. 6.

both structures. Table 2 gives an illustration of the temperature course of isomerism contributions to enthalpy, entropy, and heat capacity.

As already mentioned, the energetics of the two isomers is available [6] in two different approximations. In either of the two cases, the $\delta C_{p,1}^{(iso)}$ term exhibits a sharp temperature maximum as shown in Table 3. If we abandon the approximations to energy, the energy difference between both isomers can be taken as a free variation parameter (z -variation), $z = \Delta H_{0,2}^\ominus - \Delta H_{0,1}^\ominus$, and its value which yields the highest maximum in the $\delta C_{p,1}^{(iso)}$ term can be found

$$\frac{\partial \delta C_{p,1}^{(iso)}}{\partial z} = 0 \quad (4)$$

Table 3 shows that the MP2 and MP3 maxima are not too far from the highest value obtained within the variation treatment.

In conclusion, it can be stated that isomerism contributions to heat capacity found with the $(CO_2)_2^-(g)$ system show that isomerism effects could have a surprisingly large influence on cluster thermodynamics.

TABLE 2

Temperature dependences of the isomerism contributions^a to enthalpy $\delta H_{D_{2d}}^{(iso)}$, entropy $\delta S_{D_{2d}}^{(iso)}$, and heat capacity $\delta C_{p,D_{2d}}^{(iso)}$ of $(CO_2)_2^-(g)$ related to the D_{2d} structure^b

T (K)	MP2			MP3		
	$\delta H_{D_{2d}}^{(iso)}$	$\delta S_{D_{2d}}^{(iso)}$	$\delta C_{p,D_{2d}}^{(iso)}$	$\delta H_{D_{2d}}^{(iso)}$	$\delta S_{D_{2d}}^{(iso)}$	$\delta C_{p,D_{2d}}^{(iso)}$
200	1×10^{-3}	6×10^{-3}	0.1	0.2	1.3	14.0
298.15	0.4	1.3	14.3	7.5	29.1	127.7
400	6.3	17.6	112.6	16.9	56.7	47.9
500	18.7	45.5	106.0	19.5	62.8	13.4
600	25.8	58.5	41.8	20.3	64.3	5.0

^a H term in kJ mol^{-1} , otherwise in $\text{J K}^{-1} \text{mol}^{-1}$.

^b See Table 1.

TABLE 3

Temperature positions (T_{\max}) of the maxima in isomerism contributions to heat capacity $\delta C_{p,1,\max}^{(\text{iso})}$ in the $(\text{CO}_2)_2^-(\text{g})$ isomeric system ^a

Source	$\Delta H_{0,2}^\ominus - \Delta H_{0,1}^\ominus$ (kJ mol ⁻¹)	T_{\max} (K)	$\delta C_{p,1,\max}^{(\text{iso})}$ (J K ⁻¹ mol ⁻¹)
MP2	26.1	442.4	133.7
MP3	16.5	300.2	127.8
z-variation	53.0 ^b	830.9	136.1

^a 1, D_{2d} ; 2, C_s ; see Table 1.

^b An optimal value of the term leading to the highest $\delta C_{p,1,\max}^{(\text{iso})}$ term, see eqn. (4).

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